Effects of vacancy structural defects on the thermal conductivity of silicon thin films*

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Abstract: Vacancy structural defect effects on the lattice thermal conductivity of silicon thin films have been investigated with non-equilibrium molecular dynamics simulation. The lattice thermal conductivities decrease with increasing vacancy concentration at all temperatures from 300 to 700 K. Vacancy defects decrease the sample thermal conductivity, and the temperature dependence of thermal conductivity becomes less significant as the temperature increases. The molecular dynamics result is in good agreement with the theoretical analysis values obtained based on the Boltzmann equation. In addition, theoretical analysis indicates that the reduction in the lattice thermal conductivity with vacancy defects can be explained by the enhanced point-defect scattering due to lattice strain.

Key words: molecular dynamics simulation; vacancy defects; thermal conductivity; silicon

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1. Introduction

As the dimensions of electronic and mechanical devices are approaching the nanometer scale, the thermal conductivity of thin films is of crucial importance to both performance and function. However, the experimental measurement of thermal conductivity becomes quite difficult for nanometer scale devices because typically the contributions of individual defects cannot be deconvoluted. To predict the thermal properties of nano-scale materials and devices, it has been suggested that reliable theoretical and computational methods must be developed. Molecular dynamics (MD) simulations have become a powerful tool for the study of thermal transport at the nanoscale. With MD, the thermal conductivity can be calculated from equilibrium calculations, a known heat flux and temperature gradient, or temperature decay calculations. The MD simulations of thermal conductivities of thin films have been reported[1−3]. These simulations have shown that the thermal conductivities of nano-scale films are lower than the bulk value and that they depend on the film thickness and temperature. This phenomenon is explained as phonons (nuclear vibrations) and phonon scattering.

Vacancies are the most common defects in thin films, and have drawn much research attention in recent years. MD simulation is also best suited to studying the effects of structural imperfections on the thermal conductivity. Liu *et al.*[4] used MD simulations to research the effects of film size and vacancy defect effects on the thermal conductivities of argon thin films, and their results showed the existence of phonon boundary scattering; Lauwaer *et al.*[5] recently measured the thermodynamic properties of intrinsic point defects in germanium by MD simulation and found that the vacancy diffusivity did not lead to realistic vacancy cluster distributions. In the present study, results are presented on the simulation of the effect of vacancy structural defects in silicon thin films via molecular dynamics calculations. These results are observed to mutually agree with theoretical calculations based on the Boltzmann equation.

2. Simulation methodology

Thermal conductivities can be calculated using either equilibrium molecular dynamics (EMD) or non-equilibrium molecular dynamics (NEMD). EMD simulation, based on the Green–Kubo formulation, uses current fluctuations to calculate the thermal conductivity at a constant temperature; NEMD is a direct simulation method that is based on imposing a heat flux and subsequently measuring thermal conductivity using the classical Fourier law of thermal conduction. The NEMD approach is analogous to the experimental measurements of heat conduction and is preferred over the EMD-based approach to compute the thermal conductivity of inhomogeneous material systems. We use the NEMD-based approach in our analyses.

Figure 1 shows the MD simulation model in the present research. The positions of unit cells are initialized according to the crystal lattice structure. In the thickness direction, the x-direction, the domain is divided into heating, cooling, and conducting zones where the velocities of all atoms are controlled to maintain the desired temperature. In addition, adiabatic regions are also incorporated along the x direction where atoms

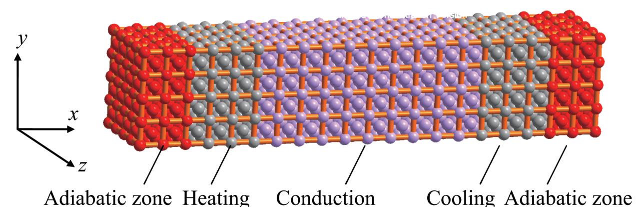

Fig. 1. MD simulation model.

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Table 1. Parameters for Si Tersoff potential.

D_e (eV)	R_e (nm)	β (nm^{-1})	S	a	n	δ	c	d	h	R (nm)	D (nm)
2.6660	0.2295	14.656	1.4316	1.1000×10^{-6}	7.8734×10^{-1}	$1/(2n)$	1.0039×10^{5}	16.217	–0.59825	0.285	0.015

are stationary, so the velocities of each atom in this region are 0. Periodic boundary conditions imposed in the y and z directions and 4×4 unit cells are chosen in the transverse direction cross-sectional area. The vacancy defective systems are constructed by removing atoms and the positions of the atoms removed are selected randomly from the cells.

Tersoff[6] proposed a many-body potential function for silicon, carbon, germanium and combinations of these atoms. For simulations of silicon thin films, this potential is widely used. The Tersoff potential is written as

$$\Phi = \sum_{i} \sum_{j(i \neq j)} f_c(r_{ij}) \left[V_R(r_{ij}) - b_{ij}^{*} V_A(r_{ij}) \right]. \quad (1)$$

In this expression, $V_R(r)$ and $V_A(r)$ are repulsive and attractive parts of the Morse type potential, respectively.

$$V_R(r_{ij}) = f_c(r) \frac{D_e}{S-1} \exp\left[-\beta \sqrt{2S}(r - R_e) \right], \quad (2)$$

$$V_A(r_{ij}) = f_c(r) \frac{D_e S}{S-1} \exp\left[-\beta \sqrt{2/S}(r - R_e) \right]. \quad (3)$$

The cutoff function $f_c(r)$ is a simple decaying function centered at $r = R$ with a half width of D.

$$f_c(r) = \begin{cases} 1, & r \leqslant R - D, \\ \frac{1}{2} - \frac{1}{2} \sin\left[\frac{\pi}{2}(r - R)/D \right], & R - D < r < R + D, \\ 0, & r \geqslant R + D. \end{cases} \quad (4)$$

Finally, the b_{ij}^{*} term expresses the modification of the attractive force $V_A(r)$ depending on θ_{ijk}, the bond angle between bonds $i - j$ and $i - k$.

$$b_{ij}^{*} = \frac{b_{ij} + b_{ji}}{2}, \; b_{ij} = \left\{ 1 + a^n \left[f_c(r_{ik}) g(\theta_{ijk}) \right]^n \right\}^{-\delta}, \quad (5)$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2}. \quad (6)$$

The parameter constants for Tersoff potential for silicon are listed in Table 1.

According to the classical Boltzmann statistic, the temperature of each layer was calculated using the formula

$$\frac{1}{2} \left\langle \sum_{i=1}^{N} m_i v_i^2 \right\rangle = \frac{3}{2} N k_B T, \quad (7)$$

where $\langle \cdots \rangle$ denotes the statistical average over the simulation time and N is the number of atoms in the layer. However, classical statistic exists only when the temperature is much higher than the Debye temperature and hasn't a relation with the thermal region temperature. If T is less than the Debye temperature, quantum correction needs to be applied to get the real temperature T of every layer.

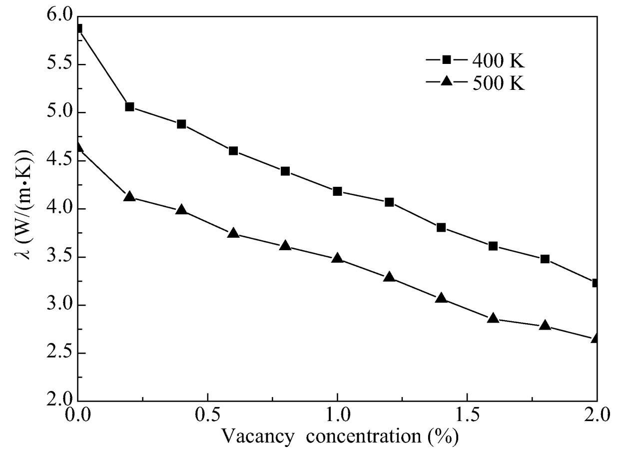

Fig. 2. Thermal conductivity of 5.43 nm thick Si film as a function of vacancy concentration.

The heat flux was calculated from the change in the kinetic energy of the hot and cold atoms,

$$\Delta E = \frac{1}{2} m \sum_{i=1}^{N} (v_{i,\text{new}}^2 - v_{i,\text{old}}^2). \quad (8)$$

Based on the Fourier law, the thermal conductivity of the silicon thin film is

$$\lambda = \frac{\Delta E_{\text{hot}} + \Delta E_{\text{cool}}}{2\tau A \langle \nabla T \rangle}, \quad (9)$$

where τ is the simulation step time; A is the cross-sectional area; ∇T is the absolute value of the temperature gradient in the cross-plane direction; and ΔE_{hot} and ΔE_{cool} represent the energy added and removed in the hot and cool regions, respectively.

3. Simulation results and discussion

A microcanonical ensemble (NVE) was employed for the simulations. The total time steps were 5×10^6 and a time step of 1 fs was used in the simulations. After the first 10^6 steps of simulation, which were used to relax the system to equilibrium, the data were gathered for statistical analysis.

Figure 2 shows the computed thermal conductivities of 5.43 nm thick silicon thin films at 400 and 500 K with the vacancy concentration ranging from 0 to 2%. As shown, the thermal conductivity decreases rapidly with increasing vacancy concentration. For the perfect sample, the thermal conductivity is 5.875 W/(m·K) at a temperature of 400 K, but the thermal conductivity of the film with 0.2% vacancy defects decreases by about 14%. The thermal conductivity of the film at 400 K is larger than that at 500 K with the same vacancy concentration. Figure 3 shows that the computed thermal conductivities

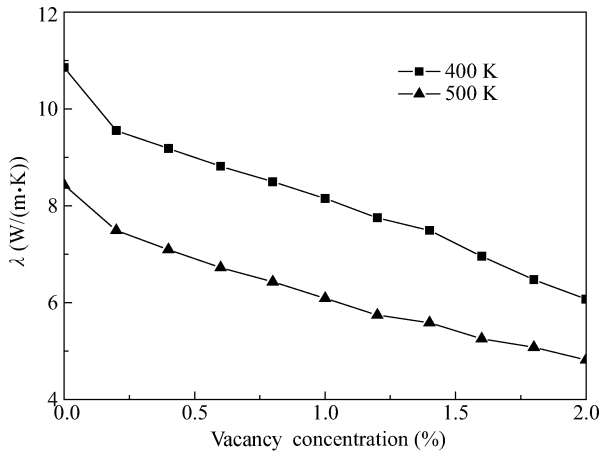

Fig. 3. Thermal conductivity of 10.86 nm thick Si film as a function of vacancy concentration.

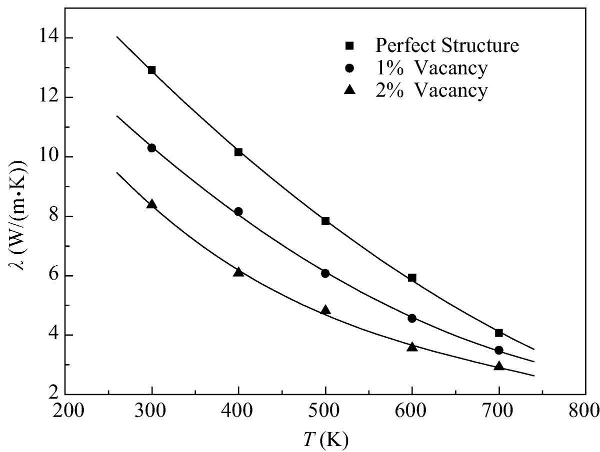

Fig. 4. Thermal conductivity as a function of temperature.

of 10.86 nm thick silicon thin films at 400 and 500 K also decreases with the increase in vacancy concentration and this variation tendency is concordant with the 5.43 nm thick silicon thin films. The thermal conductivities of the 10.86 nm thick thin film are larger than that of 5.43 nm thick thin film with the same vacancy concentration, which is also the same as the effects of different thicknesses on the thermal conductivities of pure film. Our calculations indicate that vacancy defects make a very big contribution to the decline of thermal conductivity, and optical phonons have a big effect on the values of the thermal conductivity.

Figure 4 shows the vacancy effects on the thermal conductivity of 10.86 nm thick silicon thin films over the temperature range of 300–700 K. The simulation results show that vacancy defects decrease the sample thermal conductivity and the temperature dependence of thermal conductivity becomes less significant as the temperature increases. In addition, the rate of change of thermal conductivity with the increase in vacancy concentration is smaller for films of high temperature.

To confirm that MD simulation can provide accurate results for the thermal conductivity of semiconductor thin films with vacancy defects, we also base the theoretical analysis on the Boltzmann equation applied to silicon thin films to investigate the effects of vacancy defects on the thermal conductivity. The phenomenological model developed by Callaway[10] is a useful approach to predict the thermal conductivity of bulk solids. The lattice thermal conductivity in Callaway theory can be calculated using the following expression,

$$\lambda = \frac{k_{\mathrm{B}}\omega_{\mathrm{D}}^{3}}{2\pi^{2}v}\left(\frac{T}{\theta}\right)^{3}\int_{0}^{\theta/T}\frac{x^{4}\mathrm{e}^{x}}{(\mathrm{e}^{x}-1)^{2}}\tau(\omega)\mathrm{d}x, \tag{10}$$

where k_{B} is the Boltzmann constant, ω_{D} and θ are the Debye frequency and temperature, which is 675 K for silicon, T is the absolute temperature, v is the speed of sound, τ is the overall relaxation time, and $x = h\omega/k_{\mathrm{B}}T$ is a dimensionless quantity.

Generally, the reduction in the lattice thermal conductivity can be realized employing the following major processes: the normal three-phonon scattering, point-defect scattering, boundary scattering, and phonon Umklapp scattering. So the phonon scattering relaxation rate τ^{-1} is equal to

$$\tau^{-1} = \tau_{\mathrm{N}}^{-1} + \tau_{\mathrm{D}}^{-1} + \tau_{\mathrm{B}}^{-1} + \tau_{\mathrm{U}}^{-1}. \tag{11}$$

The relaxation time due to the boundary scattering depends on the phonon group velocity and the characteristic grain size L. So it can be expressed as

$$\tau_{\mathrm{B}}^{-1} = v/L. \tag{12}$$

The inverse lifetimes of three-phonon scattering and Umklapp scattering processes are defined as

$$\tau_{\mathrm{N}}^{-1} + \tau_{\mathrm{U}}^{-1} = (B_1 + B_2)\omega^2 T^3. \tag{13}$$

The relaxation time due to point-defect scattering can be written as

$$\tau_{\mathrm{D}}^{-1} = A\omega^4. \tag{14}$$

In pure materials, the normal three-phonon and Umklapp processes dominate and impurity and boundary scattering processes contribute little to the thermal resistance, thus B_1 and B_2 can be deduced from the experimental data for perfect Silicon films. The coefficient A depends on the defect concentration and it can be formed from

$$A = \frac{V_0}{4\pi v^3}\sum_i f_i\left[1-\left(\frac{M_i}{M}\right)\right]^2, \tag{15}$$

where V_0 is the atomic volume, M_i is the mass of an atom, M is the average mass of all atoms, and f_i is the fraction of atoms with mass M_i.

The thermal conductivity of silicon film with vacancy defects can be calculated according to the above equations. Figures 5 and 6 show a comparison between theoretical predictions and the molecular dynamics simulation results of 5.43 nm thick silicon film at 400 K and 500 K. It can be found from Figs. 5 and 6 that the results of the theoretical model and the molecular dynamics simulation are in good agreement in the variation tendency, which shows that the thermal conductivities decrease significantly with increasing vacancy concentration. Theoretical analysis also shows that the major part of the lattice thermal conductivity reduction is associated with strain field fluctuations which cause the point-defect scattering. Although the results of molecular dynamics simulation are a little lower than the results of the lattice dynamics model, they also indicate that the fitting of molecular dynamics simulation results is a viable alternative to direct calculation.

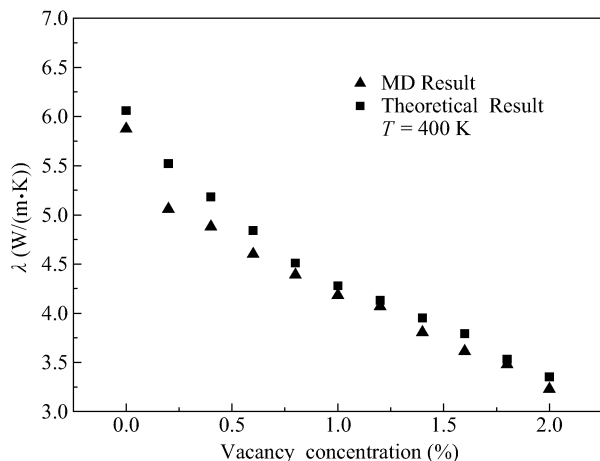

Fig. 5. Comparison between the results of MD simulation and theoretical analysis at 400 K.

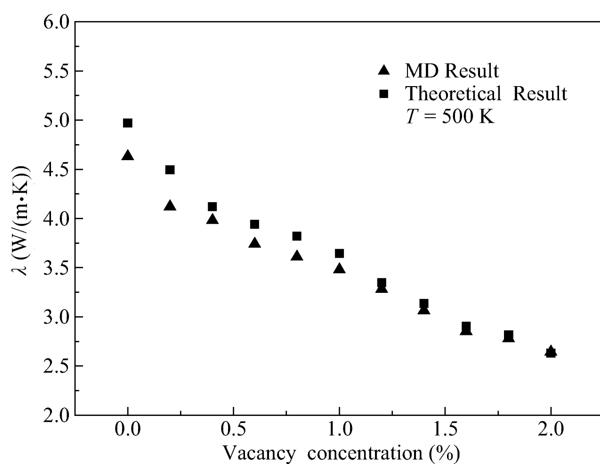

Fig. 6. Comparison between the results of MD simulation and theoretical analysis at 500 K.

4. Conclusion

Non-equilibrium molecular dynamics simulation is used to investigate the effects of the vacancy defects on the thermal conductivity of silicon thin films. We demonstrate a significant reduction in the thermal conductivity in the temperature range of 300–700 K. The calculations indicate that vacancy defects make a very big contribution to the decline in thermal conductivity, and optical phonons have a big effect on the values of the thermal conductivity. MD simulation results fit the lattice thermal conductivity data well, which are obtained based on the Boltzmann equation. The theoretical models show that the physical mechanism of vacancy defects affecting the thermal conductivity is the phonon scattering of impurities due to lattice strain. This paper suggests a fruitful approach to reduce the lattice thermal conductivity, which may provide important guidance for future improvements in the thermoelectric figure of merit of semiconductor materials.

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